Precise *ab initio* calculations of the 3d transition-metal clusters: Sc$_2$

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The ground $^5\Sigma_u^-$ state of Sc$_2$ was studied by the valence multireference configuration interaction method with single and double excitations plus Davidson correction (MRCISD(+Q)) at the complete basis set limit. The calculations were made under C_{2v} symmetry restrictions, which allowed us to obtain at the dissociation limit the Sc atoms in different states (in all previous studies of Sc$_2$ the D_{2h} symmetry group was employed). From the Mulliken population analysis and energy calculations follows that in the ground state Sc$_2$ dissociates in one Sc in the ground state and the other in the second excited quartet state, ^{4}F$_u$. The corrected parameters of the ground potential curve are the following: $R_e = 5.2$ bohr, $D_e = 50.37$ kcal/mol, and $\omega_e = 234.5$ cm^{-1}. The dissociation energy in respect to the dissociation on two Sc in the ground states was estimated as $D_e = 9.98$ kcal/mol. *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:10.1063/1.3584201]

I. INTRODUCTION

The 3*d* transition-metal clusters have attracted a wide attention both experimentally and theoretically.[1] This great interest is associated with their important catalytic and magnetic properties. For instance, manganese systems are characterized by very unusual magnetic behavior depending on their environment.[2, 3] Solid Mn, known as *a*-Mn, is antiferromagnetic and has a very complex lattice structure with 54 atoms per unit cell, while dilute "solutions" of Mn in Cu behave like spin glasses.[4] The unusual magnetic behavior of Mn systems appears as well in the nanoscale range in the case of Mn clusters.[5–7] The electron spin resonance (ESR) studies of Mn$_2$ and Mn$_5$ in rare-gas matrices, revealed that Mn$_2$ has an antiferromagnetic ground state with S=0, whereas Mn$_5$ has a ferromagnetic ground state with all spins parallel and S=25/2.[5]

It is worth-while to mention that *ab initio* calculations of 3*d*-clusters (even dimers) are still a challenge to theorists. The main reason is that they cannot be treated by single-reference approaches, on which the modern standard methods: configuration interaction (CI), coupled cluster (CC), and Møller-Plesset perturbation theory (MPPT) are based.

As was shown by Roos *et al.*,[8] a reliable potential curve for the ground state of the Cr$_2$ dimer can be obtained only by multireference (MR) methods. Bauschlicher[9] demonstrated that in the case of Mn$_2$, the ground state wave function found at the complete active space (CASSCF) level has a pronounced multireference character. In its configuration expansion the Hartree-Fock configuration appears with the coefficient $c_o = 0.08$, while among other configurations more than 130 have coefficients $c_i > 0.05$. Thus, instead of one base configuration in the CI procedure, a large number of reference configurations must be treated equally.

In spite of only one electron in 3*d* shell; scandium clusters, as clusters of other first row transition metals, also present a challenge to theorists. Scandium clusters, even Sc$_2$, cannot be precisely treated by a single reference approach. On the other hand, the main problem is in the existence of a large

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TABLE I. Molecular states stemming from the interaction of one Sc atom in the ground ^2D_g state and one Sc atom in the excited ^4F state.

$Sc(3d4s^2; {}^2D) + a\ Sc^*(3d^24s; {}^4F_g)$		$Sc(3d4s^2; {}^2D) + z\ Sc^*(3d4s4p; {}^4F_u)$	
Triplets	Quintets	Triplets	Quintets
$^3\Sigma_g^+(2)$, $^3\Sigma_u^+(2)$	$^5\Sigma_g^+(2)$, $^5\Sigma_u^+(2)$	$^3\Sigma_g^+(3)$, $^3\Sigma_u^+(3)$	$^5\Sigma_g^+(3)$, $^5\Sigma_u^+(3)$
$^3\Sigma_g^-(3)$, $^3\Sigma_u^-(3)$	$^5\Sigma_g^-(3)$, $^5\Sigma_u^-(3)$	$^3\Sigma_g^-(2)$, $^3\Sigma_u^-(2)$	$^5\Sigma_g^-(2)$, $^5\Sigma_u^-(2)$
$^3\Pi_g(5)$, $^3\Pi_u(5)$	$^5\Pi_g(5)$, $^5\Pi_u(5)$	$^3\Pi_g(5)$, $^3\Pi_u(5)$	$^5\Pi_g(5)$, $^5\Pi_u(5)$
$^3\Delta_g(4)$, $^3\Delta_u(4)$	$^5\Delta_g(4)$, $^5\Delta_u(4)$	$^3\Delta_g(4)$, $^3\Delta_u(4)$	$^5\Delta_g(4)$, $^5\Delta_u(4)$
$^3\Phi_g(3)$, $^3\Phi_u(3)$	$^5\Phi_g(3)$, $^5\Phi_u(3)$	$^3\Phi_g(3)$, $^3\Phi_u(3)$	$^5\Phi_g(3)$, $^5\Phi_u(3)$
$^3\Gamma_g(2)$, $^3\Gamma_u(2)$	$^5\Gamma_g(2)$, $^5\Gamma_u(2)$	$^3\Gamma_g(2)$, $^3\Gamma_u(2)$	$^5\Gamma_g(2)$, $^5\Gamma_u(2)$
^3H_g, ^3H_u	^5H_g, ^5H_u	^3H_g, ^3H_u	^5H_g, ^5H_u

number of degenerate and quasi-degenerate molecular terms, which makes the calculation of Sc_2 potential curves extremely complicated.

The ground state term of Sc is ^2D_g ($4s^23d$), with the first three excited states ^4F_g ($4s3d^2$), ^2F_g ($4s3d^2$), and ^4F_u ($4s3d4p$), which are located 1.43, 1.85, and 1.96 eV above.[10] The relatively small excitation energy makes quite probable the existence of several asymptotic dissociation limits for lowest potential curves; the symmetric $Sc(^2D_g) + Sc(^2D_g)$ and the three asymmetric: $Sc(^2D_g) + Sc^*(^4F_g)$, $Sc(^2D_g) + Sc^*(^2F_g)$, and $Sc(^2D_g) + Sc^*(^4F_u)$. In the second and fourth limits the maximum total spin of the dimer is $S = 2$. Thus, for these asymptotes the Sc_2 dimer can possess $S = 0$, 1, and 2. The total number of the lowest terms having these four dissociation limits is very high and equals 270. In Table I we represent the 160 possible triplet and quintet terms arising in the second and fourth dissociation limits.

In the ESR experiments by Knight *et al.*,[11] the $^5\Sigma_u^-$ was assigned as the ground state of Sc_2. Let us stress that it was not obtained in a direct measurement. Processing their experimental data, the authors[11] made some assumptions. According to Table I, the total spin S = 2 can be only if the Sc_2 dimer is formed from one Sc in its ground state and another in the excited quartet state. Nevertheless, this quite exotic ground state was obtained in all calculations performed till the recent time, both in precise *ab initio* calculations[12–16] and in calculations by the DFT method.[17–24] The latter is in a sharp contrast with the DFT calculation of the Mn_2 dimer, for which the obtained results for the value of the total spin in the ground state are quite conflicting.[25]

The problems with spin in the density functional theory were analyzed by one of the author in Refs. 26 and 27, where a group-theoretical proof (theorem) was given that the electron density of an arbitrary N-electron system is invariant with respect to the total spin *S*. Hence, the conventional Kohn-Sham equations have the same form for all values of *S* and cannot distinguish the states with different values of the total spin. Analysis[27] of the existing DFT procedures, developed up-to-date for the calculation of spin-multiplet structure, revealed that they modify only the expression for the exchange energy and use correlation functionals (if used) not corresponding to the total spin *S* of the state.

It should be mentioned that in spite of an incorrect form of the correlation functional, the spin-multiplet procedures developed can produce for some systems quite reasonable multiplet energies due to not essential dependence of calculated multiplet structure on the correlation energy or a successful projection procedure. Probably, this takes place in the case of Sc_2. However, the considered procedures are unsafe, their predictive value will be always doubtful.

As in the case of other transition-metal dimers, precise computational results for Sc_2 can be obtained only by *ab initio* multireference (MR) methods with large basis sets. Among widely applied MR methods are the MR CISD method[28–32] often used in conjunction with the Davidson quadruple correction,[33,34] denoted as MRCISD(+Q), and the multireference average coupled functional pair (ACPF) approach.[35,36]

Till recent time, the most precise *ab initio* calculations of Sc_2 were performed by Åkeby *et al.*[14] using a multireference treatment at the ACPF level and by Suzuki *et al.*[16] at the MRCISD (+Q) level.

After these publications it became widely accepted that the ground state of Sc_2 is the quintet $^5\Sigma_u^-$ state. This was inferred also from the ESR experiments[11] and magnetic measurements.[37]

In 2008 Matxain *et al*.[38] revised the problem of the Sc_2 ground state. They stressed that at a high level only the $^5\Sigma_u^-$ quintet was studied.[14,16] Applying the quantum diffusion Monte Carlo (DMC) method,[39] Matxain *et al*.[38] obtained the triplet $^3\Sigma_u$ state more stable than the $^5\Sigma_u$ state by 0.17 eV. The authors[38] claimed that the correct ground state of scandium dimer is the triplet $^3\Sigma_u$ state, but not the quintet $^5\Sigma_u^-$ state, as was accepted in all previous investigations.

However, the calculations by Matxain *et al*.[38] did not have a sufficient level of accuracy to be reliable. The authors[38] used a relatively small basis set and checked the DMC results comparing it with CASPT2 calculation (the latter was taken as a final criteria). It should be mentioned that for transition metals the CASPT2 approach often predicts an artificial stability.[40] CASPT2 and connected with it the MRMP2 approach[41] are very sensitive to the choice of the active space. The use of non-closed active space can lead to large errors.[40] This is what happened in the calculation,[38] as was noted by the authors in Erratum.[42] Thus, the conclusion of Matxain *et al*.[38] had to be verified in a more precise calculation. This has been done in recent publications.[43,44]

In the study by Kalemos *et al*.,[43] the MRCISD(+Q)/cc-pVQZ calculations were carried out for the two competitive terms $^5\Sigma_u^-$ and $^3\Sigma_u^-$. It was established that the quintet state $^5\Sigma_u^-$ is really the ground state and the triplet state $^3\Sigma_u^-$ is located just 1 kcal/mol (0.04 eV) above. These results were qualitatively confirmed in the study by Camacho *et al*.[44] where the multireference n-electron valence state perturbation theory (NEVPT) method[45] was employed.

Thus, at present it can be safety concluded that in its ground state the dimer Sc_2 is really in the $^5\Sigma_u^-$ state and has the total spin $S = 2$, which, as we discussed above, can be only if Sc_2 is formed with one of Sc in an excited state.

In this work we performed a detailed study of the ground state of the Sc_2 dimer using the valence MRCISD(+Q) method at the complete basis set (CBS) limit. At present it is technically impossible to take into account the inner-shell correlations using the extended Dunning type basis sets at the MRCI level, meanwhile the CBS limit can be obtained only with the Dunning-type basis sets. Thus, our computations are performed at the state-of-the-art level. Special attention was paid to study the dissociation limit. For the possibility to obtain the two Sc atoms in different states, we used $\boldsymbol{C_{2v}}$ symmetry restrictions (in all previous studies of Sc_2 the $\boldsymbol{D_{2h}}$ symmetry group was used). As follows from our results, the attribution of the dissociation limit made in Refs. 43 and 44 was incorrect.

II. METHODOLOGY

A. Computational method

The wave functions were optimized by means of the Complete Active Space Self-Consistent Field (CASSCF) method.[46,47] The active space was defined by the 3*d*, 4*s* and 4*p* orbitals, making a set of 18 active orbitals and 6 active electrons, 3 from the atomic valence shells of each atom. As was discuss in Introduction, the ground state of the scandium dimer, the $^5\Sigma_u^-$ state, stems from the interaction between one ground state Sc atom and other in an excited state, therefore the calculations were done under $\boldsymbol{C_{2v}}$ symmetry constraints. The $\boldsymbol{C_{2v}}$ calculation is much more time consuming than $\boldsymbol{D_{2h}}$ one, but it allows to obtain at the dissociation limit the two Sc atoms in different states. Although, because of the identity of Sc atoms the electronic configurations of both Sc atoms should be the same, see Eq. (4) in Discussion.

The final results were obtained by the multireference internally contracted configuration interaction (MRCISD) method.[31,32] The size-inconsistency error was corrected only through the Davidson (+Q) approach[33,34] since this error in the case of Sc_2 is small; according to Table II, the quadruple Davidson corrections lead to small changes, e.g. the difference in D_e is about 0.04 eV. For the cc-pV5Z basis set, the number of configuration functions (CFs) in the reference wave functions was approximately 34 000, their corresponding valence MRCI expansions are about 1.65×10^8 CFs, which are internally contracted to 6.7×10^6 CFs. For all calculations the MOLPRO 2009 suite of programs[48] was used.

TABLE II. The dependence of the equilibrium distance, R_e (a_0), total energy, E (hartree), dissociation energy, D_e (eV), and the harmonic frequency, ω_e (cm^{-1}), on the basis set cc-pVXZ and the CBS limit for Sc$_2$ in the ground state, $^5\Sigma_u^-$.

Basis	MRCI				MRCI(+Q)			
Set	R_e	E	D_e	ω_e	R_e	E	D_e	ω_e
TZ	5.202	-1519.567779	2.073	222.6	5.214	-1519.569566	2.111	223.6
QZ	5.195	-1519.570613	2.107	224.5	5.206	-1519.572522	2.150	224.8
5Z	5.193	-1519.571661	2.122	226.3	5.204	-1519.573631	2.166	229.2
CBS					5.200	-1519.574560	2.183	234.5

We employed the Dunning-type basis sets (see Ref. [49]) presented in the Pacific Northwest National Laboratory basis set website.[50] To study the dependence of calculation results on the basis set size and finding the complete basis set (CBS) limit, we performed calculations with three basis sets, cc-pVXZ with $X = 3$, 4, and 5. The largest basis set, cc-pV5Z, is constructed with [28s20p12d4f3g2h1i] functions, which are contracted to [9s8p6d4f3g2h1i], and comprises 153 contracted spherical gaussian functions. The scalar relativistic calculations were obtained at both calculated levels, CASSCF and MRCI, by means of the Douglas-Kroll-Hess approach in the second order scheme,[51] which is corrected in Ref. [52], and with the relativistic basis set cc-pV5Z-DK.[49]

B. Complete basis set limit

After the development by Dunning[53] of the correlation-consistent cc-pVXZ basis sets, it was recognized that the sequence of results obtained with different XZ allows an extrapolation to the CBS limit.[54–56] Calculation of E_X with different values of X makes it possible to find the CBS limit, E_∞, using some analytical function of X connecting E_X and E_∞. At present, several asymptotic formulae for finding the CBS limit at the HF, CASSCF, and MRCI levels have been developed (see Ref. [57] and references therein).

For obtaining the CBS limit at the MRCI level we applied the procedure, based on the presentation of E^{MRCI} as two terms,

$$E^{MRCI} = E^{CAS} + E^{dc}, \qquad (1)$$

and finding the CBS limit for each term separately;[57] see also previous publications.[58,59]

As we see from Eq. (1), the energy obtained at the MRCI level includes some additional electron correlation energy, E^{dc}, in comparison with the CASSCF energy. This energy is named the *external* or *dynamical correlation energy*;[57,60] it arises from the non-specific instantaneous correlation motion of electrons and was introduced by Oktay Sinanoĝlu.[61,62] At that time the MRCI approach was not created. Later Brown and Truhlar[60] divided the dynamical correlations into core and valence contributions. The latter corresponds to the dynamical correlation energy defined by Eq. (1).

For energy at the CASSCF level we used the Karton-Martin[63] extrapolation formula

$$E_X^{CAS} = E_\infty^{CAS} + A(X+1)e^{-b\sqrt{X}}, \qquad (2)$$

in which A and b are parameters found after solving equations and E_∞^{CAS} is the quantity sought for. Inserting in Eq. (2) the energy E_X^{CAS} calculated for $X = 3$, 4, and 5, we obtain three equations for three unknowns: A, b, and E_∞^{CAS}, which can be precisely solved. It should be mentioned that in the original work by Karton-Martin[63] the parameter b was optimized on a great number of simple molecules with light atoms. They recommended $b = 9$. Since our dimer consists of the 3d transition-metal atoms, we put b as a free parameter. We found that $b = 5.925$ gives better results than $b = 9$.

The CBS limit for the dynamic correlation energy, E_∞^{dc}, was found using the USTE scheme developed by Varandas.[57] The employed equation has the following form:

$$E_X^{dc} = E_\infty^{dc} + \frac{A_3}{(X - 3/8)^3}\left[1 + \frac{1}{(X - 3/8)^2}\left(\frac{a}{A_3} + cA_3^{1/4}\right)\right] \qquad (3)$$
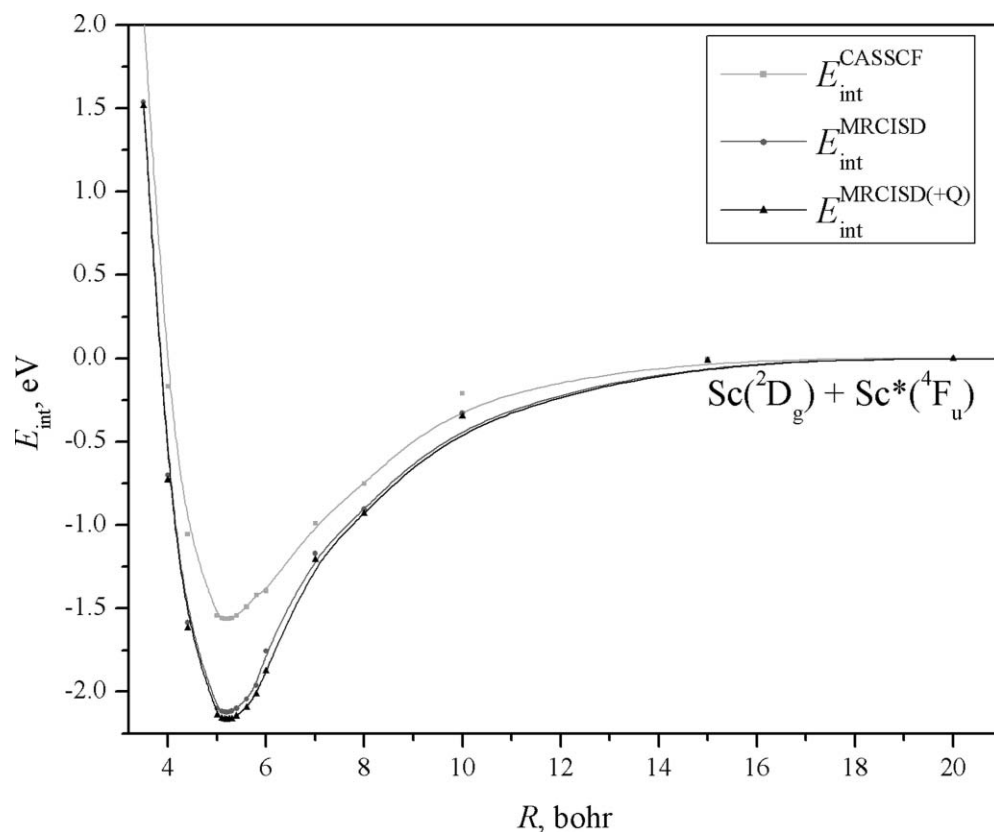
FIG. 1. Potential energy curves for the ground state of Sc_2 at the CASSCF, MRCISD, and MRCISD (+Q) levels calculated with cc-pV5Z basis set.

where a and c are fixed numerical coefficients and A_3 is a parameter that has to be found. So Eq. (4) has two unknowns, E_∞^{dc} and A_3. They were found using a code, which is based on the least-squares method, and was kindly presented to us by Varandas. The best results were obtained for the basis set pair with the highest XZ, $X = 4$ and 5.

III. RESULTS AND DISCUSSION

The dependence of obtained results on the basis set is presented in Table II. The CBS limit data are also included. We also calculated at the CBS limit the harmonic part of the ground state potential curve and found all spectroscopic parameters by the Dunham analysis.[64] According to Table II, the larger is the basis set the stronger is the bonding. The dissociation energy D_e at the CBS limit is equal to 2.183 eV (50.3 kcal/mol). The obtained equilibrium distance at the MRCISD(+Q)/CBS level is equal to $R_e = 5.2$ bohr (2.752 Å). Taking account for the $3s3p$ inner-shell correlation effects at the RCCSD(T)/cc-pVQZ level in our previous study[43] did not change D_e, but reduced R_e on 0.2 bohr. Thus, the value of R_e should be diminished on about 0.2 bohr. The harmonic frequency ω_e, at the MRCISD(+Q)/CBS level, is equal to 234.5 cm^{-1}, which is in a very good agreement with the experimental value 239.9 cm^{-1}.[65]

The potential energy curves of Sc_2 in the ground state $^5\Sigma_u^-$, calculated at the CASSCF, MRCISD, and MRCISD(+Q) levels with the largest basis set cc-pV5Z, are represented in Fig.1. The last two curves almost coincide (in the hartree scale). This fact and the data in Table II for the equilibrium distance indicate that in the case of Sc_2 the size-inconsistency error is small, in contrast to the Mn_2 dimer case.[25] Thus, the MRCISD(+Q) approach can be considered as a quite satisfactory approximation for the study of the Sc_2 dimer.

TABLE III. Comparison of the dissociation energy, D_e, and harmonic frequency, ω_e, for the Sc_2 ground state potential curves calculated at the scalar relativistic level with cc-pV5Z-DK basis set and the nonrelativistic MRCISD(+Q) level with the basis set cc-pV5Z; energies are in eV (kcal/mol), frequencies are in cm^{-1}.

Basis set	CASSCF		MRCISD		MRCISD(+Q)	
	D_e	ω_e	D_e	ω_e	D_e	ω_e
5Z	1.563 (36.01)	217.1	2.122 (48.90)	226.3	2.166 (49.91)	229.2
5Z-DK	1.578 (36.37)	223.9	2.127 (49.01)	229.0	2.169 (49.98)	229.1

TABLE IV. Mulliken population in Sc_2 at the equilibrium and dissociation limit distances at different levels of theory.

a) MRCISD

R_e:
$$4s^{1.22}3d^{1.29}4p^{0.46}{:}4s^{1.22}3d_{z^2}^{0.49}3d_{x^2-y^2}^{0.01}3d_{xz}^{0.39}3d_{yz}^{0.39}3d_{xy}^{0.01}4p_z^{0.22}4p_x^{0.12}4p_y^{0.12}$$

$R = 50a_0$:
$$Sc\left(4s^23d^1\right):4s^{1.82}3d_{z^2}^{0.01}3d_{x^2-y^2}^{0.00}3d_{xz}^{0.01}3d_{yz}^{0.01}3d_{xy}^{0.98}4p_z^{0.05}4p_x^{0.05}4p_y^{0.05}$$
$$Sc\left(4s^13d^14p^1\right):4s^{0.95}3d_{z^2}^{0.02}3d_{x^2-y^2}^{0.99}3d_{xz}^{0.01}3d_{yz}^{0.01}3d_{xy}^{0.00}4p_z^{0.98}4p_x^{0.01}4p_y^{0.01}$$

b) CASSCF

R_e:
$$4s^{1.22}3d^{1.26}4p^{0.47}:4s^{1.22}3d_{z^2}^{0.48}3d_{x^2-y^2}^{0.01}3d_{xz}^{0.38}3d_{yz}^{0.38}3d_{xy}^{0.01}4p_z^{0.23}4p_x^{0.12}4p_y^{0.12}$$

$R = 50a_0$:
$$Sc\left(4s^23d^1\right):4s^{1.82}3d_{z^2}^{0.00}3d_{x^2-y^2}^{0.50}3d_{xz}^{0.00}3d_{yz}^{0.00}3d_{xy}^{0.49}4p_z^{0.06}4p_x^{0.05}4p_y^{0.05}$$
$$Sc\left(4s^13d^14p^1\right):4s^{0.96}3d_{z^2}^{0.02}3d_{x^2-y^2}^{0.50}3d_{xz}^{0.01}3d_{yz}^{0.01}3d_{xy}^{0.50}4p_z^{0.98}4p_x^{0.01}4p_y^{0.01}$$

In Table III the scalar relativistic calculations carried out with the cc-pV5Z-DK basis set are compared with nonrelativistic MRCISD(+Q) calculations performed with the cc-pV5Z basis set at the same equilibrium distance, R_e, which does not change at the relativistic level. As follows from Table IV, the difference in the dissociation energy, D_e, in comparison with the value obtained at the nonrelativistic level, is very small; at the CASSCF level it equals 0.36 kcal/mol and at the MRCISD(+Q) level it is only 0.07 kcal/mol. The change of the harmonic frequency, ω_e, is also small; at the CASSCF level it equals 6.8 cm^{-1} and at the MRCISD(+Q) level it is reduced up to 0.1 cm^{-1}. The small values of the relativistic corrections for the $3d$-transition metals can be expected.[49,66] This is the reason why we did not take into account the spin-orbit effects and other relativistic corrections.

The determination of the dissociation limit of the Sc_2 ground state potential curve is a rather delicate problem. From the experiment[11,37] and precise calculations (see discussion in Introduction) it follows that the Sc_2 ground state corresponds to the $^5\Sigma_u^-$ term, which can be obtained if one of Sc atoms is created in an excited quartet state. Only in this case the total spin S of Sc_2 can be equal 2. But according to Table I, the quintet term $^5\Sigma_u^-$ can have two dissociation limits: $Sc(^2D_g) + Sc^*(^4F_g)$ and $Sc(^2D_g) + Sc^*(^4F_u)$. In both limits Sc_2 dissociates in one Sc in the ground state and another in an excited state, ^4F_g or ^4F_u. For obtaining two Sc in different state we employed the C_{2v} symmetry restrictions. Although, in the wave function, describing the dissociation limit, both scandium atoms should have the same population, see discussion below.

In Table IV the Mulliken atomic valence orbital populations at the equilibrium, R_e, and dissociation limit, $R = 50$ bohr, distances are represented. From it follows that at the MRCISD(+Q) level, Sc_2 dissociates on one Sc in the ground state, Sc ($4s^23d^1$; ^2D_g), and another in the second excited quartet state, Sc* ($4s^13d^14p^1$; ^4F_u). The same dissociation limit is obtained at the CASSCF level.

Thus, the Mulliken population indicates that the ground state potential energy curve of Sc_2 has the asymmetric $Sc(^2D_g) + Sc^*(^4F_u)$ dissociation limit. On the other hand, both Sc atoms are identical and each of them can be excited. So, at the dissociation limit the wave function of the dimer must be a linear combination of the wave function, in which one Sc atom is in the ground state and another Sc atom is in an excited state, and the wave function describing the opposite possibility:

$$\Psi\left(Sc_2, R \to \infty\right) = \frac{1}{\sqrt{2}}\left[\Psi_0\left(Sc_a\right)\Psi_n\left(Sc_b^*\right) + \Psi_n\left(Sc_a^*\right)\Psi_0\left(Sc_b\right)\right]. \tag{4}$$

TABLE V. Comparison of the dissociation limit energy of Sc_2 in the ground state and energies of the Sc atom in the ground and excited states calculated with the basis set cc-pV5Z at different levels of theory; energies are in hartree, Δ is in kcal/mol.

	CASSCF	MRCISD	MRCISD+Q
$Sc_2(R = 50a_0)$	-1519.476420	-1519.493675	-1519.494029
$Sc(^2D_g) + Sc^*(^4F_g)$	-1519.465245	-1519.498898	-1519.508093
$Sc(^2D_g) + Sc^{**}(^4F_u)$	-1519.467668	-1519.493072	-1519.494483
Δ (^4F_g)[a]	7.01	3.27	8.82
Δ (^4F_u)[b]	5.5	0.38	0.28

[a] Δ (^4F_g) = $Sc_2(R = 50a_0)$ - [$Sc(^2D_g) + Sc^*(^4F_g)$]
[b] Δ (^4F_u)[b] = $Sc_2(R = 50a_0)$ - [$Sc(^2D_g) + Sc^{**}(^4F_u)$]

TABLE VI. CBS D_e values with relativistic corrections for two dissociation limits; energies are in eV (kcal/mol).

Method	D_e $^2D_g + {}^4F_u$	D_e $^2D_g + {}^2D_g$
CASSCF	1.58 (36.40)	-0.196 (-4.52)
MRCISD(+Q)	2.186 (50.37)	0.433 (9.98)

This reflects the quantum-mechanical indistinguishability of identical atoms. As a result, both Sc atoms have an equal population: $4s^{1.5}3d^14p^{0.5}$.

The dissociation on one of the atoms in the second, but not in the first, excited quartet state seems quite unusual. For verifying this result we have compared the dimer energy at $R = 50$ bohr with the sum of atomic energies of different excited quartet states calculated at the same level of theory. As follows from Table V, the energy of Sc_2 at $R = 50$ bohr corresponds to the sum of energies $Sc(^2D_g) + Sc^*(^4F_u)$. The dissociation level $Sc(^2D_g) + Sc^*(^4F_g)$ is located on 0.0141 hartree (or 8.82 kcal/mol) below, which is much larger than the calculation error. At the CASSCF level we cannot arrive to definite conclusions using the atomic energy calculations.

We would like to note that in our recent study[43] of $^5\Sigma_u^-$ state with the $\boldsymbol{D_{2h}}$ symmetry restriction, the $Sc(^2D_g) + Sc^*(^4F_u)$ dissociation limit was obtained. Nevertheless, it was rejected as a wrong asymptote and the creation of one of Sc in ^4F_g state was postulated. Camacho *et al.*,[44] based on an almost negligible $4p$ population obtained in their studies, also made the erroneous conclusion that at the dissociation limit Sc does not appear in the ^4F_u state. On the one hand, a negligible $4p$ population obtained in Camacho *et al.* studies[44] indicates that the NEVPT method does not give a reliable Mulliken population. On the other hand, from the population of excited orbitals at the equilibrium distance it may not be done any conclusion about the population at the dissociation limit. The interatomic interactions at the equilibrium distance can populate excited orbitals, although this does not prevent atoms to dissociate in their ground states. Precisely, this takes place in the case of the alkaline-earth dimers.[67]

Thus, a more detailed analysis performed in the present study demonstrates that the conclusions about the dissociation limit of the Sc_2 ground state potential curve made in Refs. 43 and 44 were not properly substantiated.

The values of the dissociation energy, D_e, obtained at the CBS limit and corrected on the scalar relativistic effects are presented in Table VI. For obtaining D_e at the symmetric dissociation limit Sc (^2D_g) + Sc (^2D_g), the calculated atomic excitation energy E [Sc* (^4F_u)] – E [Sc (^2D_g)] was subtracted from D_e obtained in the dissociation limit Sc (^2D_g) + Sc* (^4F_u). At the CASSCF level the negative value of D_e for the symmetric dissociation limit was obtained. This is connected with a lack of precision for calculating the atomic excited states at this level.

When atoms are approaching, the atomic orbital population is redistributed between atoms. The Mulliken analysis (even at the $\boldsymbol{C_{2v}}$ symmetry restrictions) gives at the equilibrium distance the same orbital population for both atoms. As follows from Table IV, the MRCISD orbital population on each atom is equal to $4s^{1.22}3d^{1.29}4p^{0.46}$. This population is favorable for the atomic hybridization.[68]

The hybrid orbitals enhance the overlap in the bond region increasing the strength of the bond. Thus, in the Sc_2 dimer there is a covalent chemical bonding in contrast with the Mn_2 dimer.[25]

IV. CONCLUSIONS

It has been demonstrated that the ground state potential curve, $^5\Sigma_u^-$, has the asymmetric dissociation limit, Sc (^2D_g) + Sc* (^4F_u) with one of the Sc atoms in the second excited quartet state. Due to the quantum-mechanical indistinguishability of Sc atoms, in the wave function describing the dissociation limit both scandium atoms have the same population.

The ground state dissociation energy at the valence MRCISD(+Q)/CBS level is equal to 2.186 eV (50.37 kcal/mol) and with respect to the thermodynamically stable dissociation limit with both Sc atoms in their ground states it is equal to 9.98 kcal/mol. The harmonic frequency $\omega_e =$ 234.5 cm^{-1} is in an excellent agreement with the experimental value 239.9 cm^{-1}.[65]

At the equilibrium distance a strong atom-atom interaction populates the $4p$ atomic orbitals, which remain populated at infinity; it transfers 0.29e on $3d$ orbitals and makes the closed $4s$ shell partly open. This favors the atomic hybridization. The Sc dimer is stabilized by the formation of one two-electron $(4s4p_z)\sigma_g$ bond and two one-electron bonds: $(3d_{xz}4p_x)\pi_{xu}$ and $(3d_{yz}4p_y)\pi_{yu}$. Thus, the Sc_2 dimer has a covalent bonding.

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